Understanding PAH/Soot Formation Chemistry in Combustion Systems

NIST's Chemical Science and Technology Laboratory in collaboration with the Building and Fire Research Laboratory have have carried out an experimental and analytical program designed to develop sufficient understanding of the combustion process so that formation of PAHs and soot can be predicted for a fuel such as heptane on the basis of simulations. This research is important because the incomplete combustion of organic fuels can lead to the formation of polyaromatic hydrocarbons (PAH) and particulate matter, which are known to have deleterious health effects. The work described here has been ongoing for a number of years and has been supported by the Department of Defense.

W. Tsang (Div 838)

Understanding the combustion process is important because the incomplete combustion of organic fuels can lead to the formation of polyaromatic hydrocarbons (PAH) and particulate matter. A longstanding aim in combustion research is to develop methods for their amelioration through combustion controls. This has become particularly important in recent years due to the stringent regulations that have or are being imposed. Thus the PM 2.5 standard can have severe effects on the type of combustors that can be used or the type of filters and catalytic converters that must be fitted into the exhaust of the combustors. More recent interest in biofuels has led to similar concerns regarding their effect on particulate matter emissions. Equally important is the need to understand the health effects of specific PAHs.

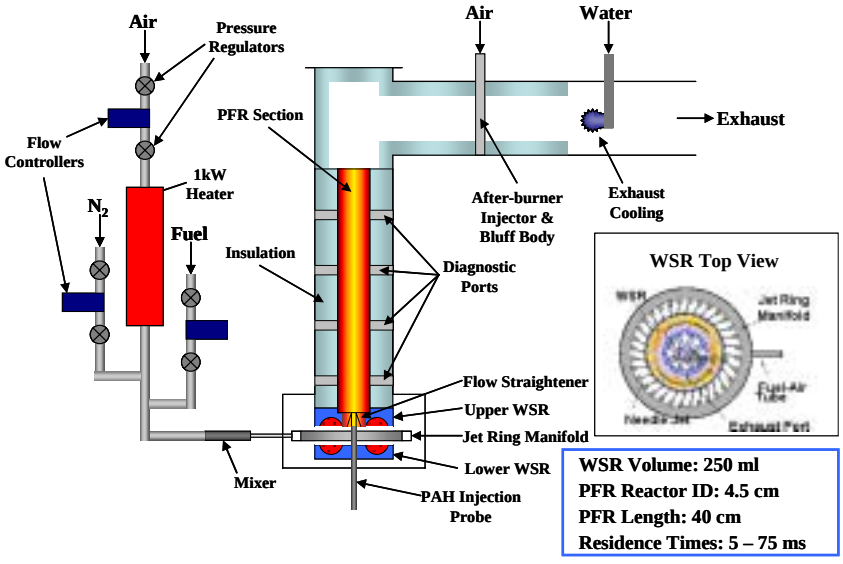
For a number of years, NIST's Chemical Science and Technology Laboratory in collaboration with the Building and Fire Research Laboratory, with the support of Strategic Environmental Research and Development Program/Department of Defense, have carried out an experimental and analytical program designed to develop sufficient understanding of the combustion process so that formation of PAHs and soot can be predicted for a fuel such as heptane on the basis of simulations. The general process for formation of PAH/SOOT involves the breakdown of the fuel to small unsaturated fragments, followed by a subsequent build-up to form larger multi-ring aromatics and ultimately particulate matter. The nature of the small unsaturated compounds determines the quantity and presumably the nature of the soot that is formed. Oxidation reactions will interrupt the progression leading to the formation of water and carbon dioxide.

The two elements in the NIST program are:

1) to develop a database to allow modeling of the combustion of heptane (a common reference fuel used in simulations) and,
2) to obtain experimental reference data to characterize the formation of PAH/SOOT.

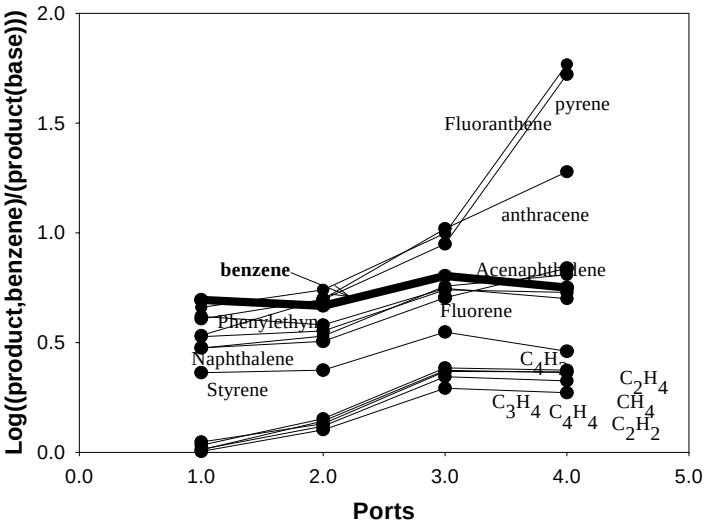
The first aspect of this program is near completion. The nature of the small unsaturated compounds has now been deduced on the basis of experiments with our heated single-pulse shock tube, evaluation of literature data, and application of theory with a NIST developed program, so that all combustion conditions can be covered. Work on PAH/SOOT formation mechanisms is being carried out. This is an intrinsically harder problem, since different compounds are being created as the reaction proceeds. In contrast, the breakdown of a fuel during combustion leads to fewer compounds and hence removes mechanistic difficulties. To characterize PAH/SOOT formation, a well stirred/plug flow reactor has been constructed.

Shown is a schematic of the NIST WSR/PFR experimental apparatus displaying the WSR/PFR assembly and detail of WSR jet ring.



The well stirred aspect of the reactor simply stretches out the flame front and leads directly to generation of reactive species and ultimately soot. The plug flow reactor gives time for the observation of the interesting chemistry preceding and during PAH and SOOT formation. Particularly interesting is the capability of introducing particular reaction intermediates into a stream of gas that has not yet began to soot, thereby inducing sooting behavior. We are now beginning to obtain information on the temporal behavior of the chemical constituents of the precursors of larger PAH and ultimately soot itself.

The figure below summarizes experimental results on the light and smaller ring PAHs that have now been detected upon the addition of small quantities of benzene into the reaction stream. This represents a comparison of yields for the case where no benzene is added. It can be seen that for the smaller unsaturates, changes are small. However the changes increase in magnitude with ring size. Clearly we are seeing an accelerating rate of ring growth. We have also made a determination through DMA size distribution. It is clear that there are important differences upon the addition of benzene. We also collect on a filter the particulate matter that is formed. These samples are being currently be analyzed in our Laboratory. Larger multi-ring aromatics have now been detected. We will also be subjecting the solid soot to TEM analysis.



Comparison of comparisons at four ports in plug flow reactor of some compounds found when 725 ppm benzene is added to system with base ethylene-air combustion. Total time between ports 1 to 4 is 45 microseconds. Temperature is 1300 K. Pressure is 1 bar. Dark line is for benzene additive.

***Impact*:** The most important short term impact is from our heptane breakdown work. Practically all existing combustion models focus on stoichiometric or near stoichiometric mixtures of fuel and oxidant. The present information should permit simulations of rich mixtures. This may be particularly important for various auto-thermal processes where the heat of reaction in a rich mixture is used to drive parallel processes during chemical conversion. It is of course also of great importance for soot formation modeling beginning with realistic fuels.

A particularly important and unexpected aspect of the work is the capability of generating well characterized soot samples with known amounts of PAHs. At the present time soot is treated as a generic material. This is probably not the case. There are significant uncertainties regarding the effects of "early" and "late" soot and controversy about the effect of various PAHs on health. The facility that we have developed has the capability of generating multi-gram quantities of such well defined material.

Future Plans: We are currently modeling the experimental results and testing the accuracy of the models that are used for making predictions regarding soot yields. Another direction of interest is to understand the effects of compounds distinct to biofuels on PAH/SOOT formation. Thus probing the behavior of phenols and methoxy ethers in a manner similar to that described for benzene will give direct information on the sooting propensity of biofuels.

Project Team:
W. Tsang, C. Stroud, and J. A. Manion (838);
S. Manzello and D. Lenhert (BFRL)